Dielectric Monitoring of Biological Cell Growth Using an Inductive Probe (INTERFACE SCIENCE-Molecular Aggregates)

AUTHOR(S):

Asami, Koji; Yonezawa, Takeshi; Wakamatsu, Hideki; Koyanagi, Naohiko

Valence Electronic Structure at the Interface of an Organic Double-Layered Thin Film

Naoki Sato

Valence electronic levels at the interfaces of a photovoltaic double-layered organic thin film prepared from *N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide) (DM-PBDCI) and chloroaluminum phthalocyanine (ClAlPc) have been examined using ultraviolet photoelectron spectroscopy (UPS). The electronic structure of a DM-PBDCI film at the interface with a substrate demonstrates notable difference between ZnO and Cu. An energetic scheme for the interface of a ClAlPc/DM-PBDCI film is proposed on the basis of the obtained results.

Keywords: Electronic structure/ Interface/ Photovoltaic cell/ Phthalocyanine / Organic double-layered thin film/

To examine if the electronic structure at the interface of a p-n junction prepared from organic semiconductors could be understood on the same basis as that from inorganic semiconductors, direct observations have been tried for the valence electronic structure in an evaporated thin film of an organic semiconductor at the interface with a conducting substrate (Cu, Au, ZnO or indium tin oxide (ITO) glass) or another organic film, using UV photoelectron spectroscopy (UPS) [1]. The system examined was a double-layered organic thin film, which has already been confirmed to show a notable photovoltaic effect [2], fabricated from *N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide) (DM-PBDCI) and chloroaluminum phthalocyanine (ClAlPc).

The UPS apparatus applied in this work was equipped with an H_2 discharge lamp attached to a VUV monochromator, used in the photon energy region from 6 to 10 eV, and also with a spherical retarding-field analyzer. Such an apparatus was useful to determine absolute energy values including work functions.

The principal experimental procedure was initial UPS measurement of a particular substrate and the cycle of the following evaporation of an organic material by several tenths-to-several nm in thickness on it with in-situ UPS measurement.

First, work functions of Cu, Au, ITO and a ZnO overlayer on ITO were determined as 4.8_2, 4.7_5, 4.1 and 3.7_4 eV, respectively. The features of UP spectra of DM-PBDCI evaporated 10 nm-thick films measured with the same excitation photon energy are almost the same for the films on Cu, Au and ZnO substrates, whereas the film on an ITO plate shows a spectrum different from the spectra of the other films. However, work functions and the threshold ionization energies observed for the films support the n-type nature of DM-PBDCI, when assumed that the energy gap of a DM-PBDCI film coincides with the energy of optical absorption edge, 2.14 eV.

While UP spectra of DM-PBDCI thin films on Cu and ZnO

INTERFACE SCIENCE —Molecular Aggregates—

Scope of research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric behaviors. The electronic structure of molecular and/or polymeric thin films is studied using photoelectron spectroscopies in connection with the former, and its results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with heterogeneous structures in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.

Prof
SATO, Naoki
(D Sc)

Assoc Prof
ASAMI, Koji
(D Sc)

Instr
KITA, Yasuo
(D Sc)

Instr
YOSHIDA,Hiroyuki
(D Sc)

Students
ENDO, Sotaro (MC)
ODA, Masao (DC)
SAKUMA, Taro (MC)
YANO, Setsuko (MC)

substrates exhibited no significant thickness dependence in the thickness range from 7 to 22 nm, those of the film on a ZnO substrate demonstrated a notable thickness dependence in the range from 1.4 to 160 nm. The principal change in the UP spectra is their apparent rigid shifts with increasing thickness, in particular, in rather thin thickness region, which suggests that the work function of the DM-PBDCI film might change with its thickness. An additional change observed for films no thicker than 10 nm is related with a clear increase of the threshold ionization energy. These observations indicate that electronic energy levels in the DM-PBDCI film at the interface with ZnO suffer from modulation being similar to the band bending at the interface of inorganic semiconductors.

The threshold ionization energy of a ClAlPc film on a Cu substrate is determined to be 5.0_4 eV, while the value of its work function is scattered within 0.4 eV centering around 4.6 eV. Assuming again that the energy gap of the ClAlPc film also coincides with the energy of optical absorption edge, 1.4 eV, the p-type nature of ClAlPc could be supported.

A ClAlPc film overlayed on a DM-PBDCI one (deposited on a Cu substrate) in the thickness of 11 nm showed the following UP spectral change: Although a small contribution from the underlayer DM-PBDCI film was observed in the spectra of ClAlPc films in the thickness less than 3 nm, the spectra of the films in the thickness range from 3 to 7 nm indicated an energy shift of the vacuum level smaller than that of the hole conduction level, and the spectra obtained for thicker (up to ~70 nm) films were almost the same as one another.

By examining the experimental results above, a schematic of energy diagram at the interface of a ClAlPc/DM-PBDCI double-layered thin film is proposed, although energy levels in the DM-PBDCI underlayer are supposed to match with those in the ClAlPc overlayer. The behaviors of the electron and hole conduction levels as well as the vacuum level in the diagram appear to be in reasonable agreement with a conclusion to be obtained from the theory on a p-n heterojunction of inorganic semiconductors. This is identical with the conclusion of our previous UPS study on organic thin film/metal interfaces [3].

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Dielectric Monitoring of Biological Cell Growth Using an Inductive Probe

Koji Asami, Takeshi Yonezawa, Hideki Wakamatsu, and Naohiko Koyanagi

A new measurement technique with an inductive probe has been developed for monitoring dielectric behavior of biological cells in fermentation, which is superior to conventional methods with regard to being free from the interference due to electrode polarization and bubble formation on electrodes.

Keywords: Dielectric measurement technique/ Biological cell suspension/ Electrode-less method/ Estimation of microbial biomass

Application of dielectric spectroscopy to the estimation of microbial biomass during fermentation was first made by Harris et al. [1]. Excellent linear relationships between the permittivity and the cell concentration (or cell mass) of cell suspensions were obtained for various cells [1,2]. In the dielectric measurements, however, we have some problems as follows: (1) The permittivity change of the fermenting broth is very small within a few hundreds in permittivity unit. Hence, we need a high precision instrument for the measurements. (2) With culture media containing electrolytes, electrode polarization causes serious errors. (3) Bubble formation at electrode surfaces interferes with the measurements. To solve these problems we have lately developed an electrode-less method [3] that is free from the electrode polarization effect and from the interference of the bubble formation on electrode surfaces. The method that is based on electromagnetic induction does not require metal electrodes but a probe that consists of two coaxial toroidal coils covered with epoxy resin (E-5050 Colloid Dielectric Probe, Hewlett-Packard). For measurements the probe is just immersed in a sample liquid, and its relative permittivity and conductivity are automatically obtained with a computer controlled Precision LCR Meter (Hewlett-Packard) over a frequency range of 100 kHz to 30 MHz. The performance of the method has been tested for beer and whisky fermentation [3]. The results demonstrated that the electrode-less method with the inductive probe provides a powerful and versatile technique for in situ and real time monitoring of cell growth in laboratory and industrial fermentation.

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